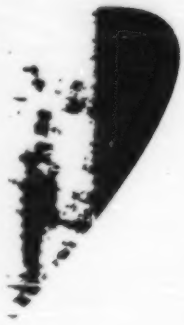

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Determination of organophosphorus chemical warfare agents and their hydrolysis products in soil by packed capillary liquid chromatography-electrospray mass spectrometry (LC-ESI-MS)

Paul A. D'Agostino, James R. Hancock and Lionel R. Provost
Defence Research Establishment Suffield

Technical Report
DRES TR 2000-075
June 2000

National Defence Défense nationale

Canada

102-00851/

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Abstract

An analytical method based on aqueous ultrasonic extraction and packed capillary LC-ESI-MS analysis was developed and compared to the existing GC-MS based method for the trace determination of organophosphorus chemical warfare agents and their hydrolysis products in contaminated soil. Three soils, a red clay, a tan sandy loam and a brown sandy clay loam, were selected and spiked with sarin and soman and their hydrolysis products, isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid, at the 10 µg/g level to assess recovery efficiency. Recovery of sarin and soman from the aqueous soil extracts was comparable to the existing analytical method, with a significant improvement in recovery being demonstrated for the chemical warfare agent hydrolysis products. Sarin and soman were recovered in the 20% to 90% range from the three soil types with aqueous extraction, while the hydrolysis products of these chemical warfare agents were extracted almost quantitatively, with recoveries in excess of 80% for all three soil types. The developed soil extraction and analysis method appears to be an attractive alternative to the GC-MS based method, since aqueous extracts containing chemical warfare agent hydrolysis products may be analysed directly, eliminating the need for additional sample handling and derivatization steps.

Résumé

Une méthode analytique basée sur l'extraction ultrasonore en milieu aqueux et l'analyse par LC-ESI-MS sur capillaire rempli a été élaborée et comparée à la méthode actuelle basée sur la CG-SM pour doser des agents chimiques organophosphorés et leurs produits d'hydrolyse présents à l'état de traces dans les sols contaminés. Trois types de sols, une argile rouge, un sable limoneux tan et une argile sableuse brune, ont été choisis et dopés avec du sarin et du soman et leurs produits d'hydrolyse, soit l'acide isopropyl-méthylphosphonique et l'acide pinacolyl-méthylphosphonique, à des niveaux de 10 µg/g, pour évaluer les taux de récupération. Les taux de récupération du sarin et du soman des extraits aqueux de sol étaient comparables à ceux obtenus avec la méthode analytique actuelle; toutefois, les taux de récupération des produits d'hydrolyse étaient nettement plus élevés. Le sarin et le soman étaient récupérés dans une proportion allant de 20 % à 90 % dans les trois types de sols par extraction en milieu aqueux, tandis que les produits d'hydrolyse étaient extraits presque quantitativement, avec des taux de récupération de plus de 80 % pour les trois types de sols. La méthode d'extraction et d'analyse des sols qui a été élaborée semble être une solution de rechange attrayante pour la méthode basée sur la CG-SM, puisque les extraits aqueux contenant les produits d'hydrolyse peuvent être analysés directement, éliminant ainsi les étapes additionnelles de manipulation d'échantillons et de dérivatisation.

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Executive summary

Introduction: The Canadian Forces (CF) may be called on to perform peacekeeping or battlefield operations in regions of the world where there is a significant threat of chemical/biological (CB) warfare agent use. To operate effectively in these theatres the CF must be able to identify the CB agent used. Mass spectrometry (MS), is a powerful analytical technique for the identification of both known and unknown compounds and DRE Suffield is currently investigating this instrumental technique in fulfilment of CF detection and identification requirements.

Results: An analytical method based on aqueous ultrasonic extraction and packed capillary LC-ESI-MS analysis was developed and compared to the existing GC-MS based method for the trace determination of organophosphorus chemical warfare agents and their hydrolysis products in contaminated soil. Three soils, a red clay, a tan sandy loam and a brown sandy clay loam, were selected and spiked with sarin and soman and their hydrolysis products, isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid, at the 10 μg/g level to assess recovery efficiency. Recovery of sarin and soman from the aqueous soil extracts was comparable to the existing analytical method, with a significant improvement in recovery being demonstrated for the chemical warfare agent hydrolysis products. Sarin and soman were recovered in the 20% to 90% range from the three soil types with aqueous extraction, while the hydrolysis products of these chemical warfare agents were extracted almost quantitatively, with recoveries in excess of 80% for all three soil types. The developed soil extraction and analysis method appears to be an attractive alternative to the GC-MS based method, since aqueous extracts containing chemical warfare agent hydrolysis products may be analysed directly, eliminating the need for additional sample handling and derivatization steps.

Significance: The CF may be deployed in regions of the world where there is a significant threat of chemical/biological warfare agent use. Identification of the CB agent is of importance since the results of such analyses would contribute to the development of strategic and political positions regarding future Canadian military operations and would facilitate the dissemination of technical advice to in-theatre field commanders and medical personnel.

Future Plans: The reported method would be valuable for the identification of organophosphorus chemical warfare agents and their hydrolysis products in soil samples collected by the Canadian Forces or in support of Chemical Weapons Convention challenge inspections.

D'Agostino, P.A., Hancock, J.R., Provost, L.R., 2000. Determination of Organophosphorus Chemical Warfare Agents and their Hydrolysis Products in Soil... DRES TR 2000-075, Defence Research Establishment Suffield.

Sommaire

Introduction : Les Forces canadiennes (FC) peuvent être appelées à effectuer des opérations de maintien de la paix ou des opérations sur champ de bataille dans des régions du monde où des agents chimiques/biologiques (agents CB) risquent beaucoup d'être utilisés. Pour effectuer ces opérations avec efficacité, les FC doivent être en mesure d'identifier l'agent CB utilisé. La spectrométrie de masse (SM) est une technique analytique puissante qui permet d'identifier des composés connus et inconnus. Le Centre de recherches pour la défense Suffield étudie en ce moment cette technique instrumentale pour répondre aux exigences de détection et d'identification des FC.

Résultats : Une méthode analytique basée sur l'extraction ultrasonore en milieu aqueux et l'analyse par LC-ESI-MS sur capillaire rempli a été élaborée et comparée à la méthode actuelle basée sur la CG-SM pour doser des agents chimiques organophosphorés et leurs produits d'hydrolyse présents à l'état de traces dans les sols contaminés. Trois types de sols, une argile rouge, un sable limoneux tan et une argile sableuse, ont été choisis et dopés avec du sarin et du soman et leurs produits d'hydrolyse, soit l'acide isopropyl-méthylphosphonique et l'acide pinacolyl-méthylphosphonique, à des niveaux de 10 µg/g, pour évaluer les taux de récupération. Les taux de récupération du sarin et du soman des extraits aqueux de sol étaient comparables à ceux obtenus avec la méthode analytique actuelle; toutefois, les taux de récupération des produits d'hydrolyse étaient nettement plus élevés. Le sarin et le soman ont été récupérés dans une proportion allant de 20 % à 90 % dans les trois types de sols par extraction en milieu aqueux, tandis que les produits d'hydrolyse ont été extraits presque quantitativement, avec des récupérations de plus de 80 % pour les trois types de sols. La méthode d'extraction et d'analyse des sols qui a été élaborée semble être une solution de rechange attrayante pour la méthode basée sur la CG-SM, puisque les extraits aqueux contenant les produits d'hydrolyse peuvent être analysés directement, éliminant ainsi les étapes additionnelles de manipulation d'échantillons et de dérivatisation.

Importance : Les FC peuvent être déployées dans des régions du monde où des agents chimiques/biologiques risquent beaucoup d'être utilisés. L'identification de l'agent CB est très importante, puisque les résultats de telles analyses vont contribuer à l'élaboration des positions stratégiques et politiques prises relativement aux opérations militaires canadiennes futures et vont faciliter la diffusion de conseils techniques aux commandants d'unités sur le terrain et au personnel médical.

Projets futurs : Cette méthode serait fort utile pour identifier les agents chimiques organophosphorés et leurs produits d'hydrolyse dans les échantillons de sols prélevés par les Forces canadiennes ou dans le cadre d'inspections par mise en demeure prévues par la Convention sur les armes chimiques.

D'Agostino, P.A., Hancock, J.R., Provost, L.R., 2000. Determination of Organophosphorus Chemical Warfare Agents and their Hydrolysis Products in Soil by Packed Capillary Liquid Chromatography-Electrospray Mass Spectrometry (LC-ESI-MS). CRDS TR 2000-075, Centre de recherches pour la défense Suffield.

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Introduction

Canadian Forces (CF) routinely participate in peacekeeping and battlefield operations where exposure to chemical warfare agents (or other chemicals) may occur. Under these circumstances, collection of representative samples by the CF would typically take place to confirm the identity of the chemical(s). Soil samples were recently collected by the CF after health concerns were raised over their deployment in Croatia between April 1993 and November 1995 as part of Operation Harmony. A sampling team was sent during the summer of 1999 to collect sandbag and soil samples from Canadian positions for detailed laboratory analysis. Defence Research Establishment Suffield was sent 76 soil samples, the majority of which were analysed for the presence of chemical warfare agents and their hydrolysis products as part of Operation Contact. Analyses of this type requires the use of sensitive, specific analytical methods, particularly when unambiguous proof is required for the prior presence of chemical warfare agents (1). These analytical demands are being actively addressed at Defence Research Establishment Suffield (DRES) through the development and application of new analytical methods for the detection and identification of chemical warfare agents, their hydrolysis products and related compounds.

Gas chromatography (GC) has been used extensively for the separation and identification of the chemical warfare agents (1,2), with gas chromatography-mass spectrometry (GC-MS) being used most frequently for the characterization of these compounds (3-7). Organophosphorus chemical warfare agents have been studied extensively by electron impact and chemical ionization mass spectrometry, as the use of these complementary ionization techniques facilitates the acquisition of molecular and fragmentation ion information that may be used for identification (8-10). GC separation, while suitable for the direct analysis of organophosphorus chemical warfare agent in organic extracts, is usually not preferred for the direct analysis of aqueous samples or extracts. Aqueous samples or extracts containing organophosphorus chemical warfare agents and/or their nonvolatile hydrolysis products normally require additional sample handling steps and derivatization (11-13). Water samples containing chemical warfare agents have been analysed by GC-MS following solid-phase microextraction (14) and by microcolumn liquid chromatography (LC) with flame photometric detection (15). Increasingly, researchers have developed LC-MS analytical methods to deal with the analysis of aqueous samples containing these nonvolatile hydrolysis products (16-22).

Thermospray mass spectrometry (16-19) and more recently the atmospheric pressure ionization (e.g., electrospray (ESI), ionspray and atmospheric pressure CI) techniques (20-27) have been employed for the analysis of organophosphorus chemical warfare agent hydrolysis products. Each technique may be interfaced to LC for component separation, with thermospray-MS having been largely superseded by atmospheric pressure ionization (API) for LC-MS analyses. Many of the recent applications deal with the analysis of higher molecular mass peptides or proteins by ESI-MS, a technique that has only recently been applied to analysis of chemical warfare agents in aqueous samples (28,29).

DRES developed an analytical scheme involving organic solvent extraction and trimethylsilylation for the determination of chemical warfare agent and their hydrolysis products in a variety of soils in the early 1990's (12). The analytical method was evaluated on Suffield range soil samples spiked at the 50 and 5 µg/g level with sarin, soman, mustard and the chemical warfare agent simulant, triethyl phosphate. These spiking levels were well below typical battlefield contamination levels, estimated to be in the 100 to 1000 µg/g range, based on a contamination density of 1 to 10 g/m^2 (soil density about 1 g/cm^3 and a 1 cm sampling depth). The 50 µg/g level was considered typical of soil contamination levels that might be expected hours to days after an attack, while lower levels would be typical of soil samples that had undergone weathering. Organophosphorus chemical warfare agents and triethyl phosphate were extracted most efficiently with dichloromethane with recoveries from the soils generally in the 5 to 70% range. Each spiked soil sample was also trimethylsilylated in an effort to determine the presence of chemical warfare agent hydrolysis products. This two step method was recently applied to the analysis of the Croatian soil samples with both the dichloromethane and trimethylsilyl/dichloromethane extracts being analysed by capillary column GC-MS. No evidence was found for the presence or prior presence of chemical warfare agents in any of the extracts of the Croatian soil samples collected in support of Operation Contact.

DRES recently published several LC-ESI-MS papers on the direct determination of chemical warfare agents, their hydrolysis products and related compounds in aqueous samples during a single analysis (27-29). LC-ESI-MS was an attractive alternative to GC-MS for these analyses, as both the organophosphorus chemical warfare agents and/or their hydrolysis products could be analysed directly without the need for additional sample handling and derivatization. A similar analytical advantage might be realized for the analysis of aqueous extracts of chemical warfare agent contaminated soil samples.

This paper focuses on the development of an aqueous extraction scheme for contaminated soil samples and the analysis of these extracts by packed capillary LC-ESI-MS for the presence of trace levels of organophosphorus chemical warfare agents and/or their hydrolysis products. Three different Croatian soils, a red clay, a tan sandy loam and a brown sandy clay loam, were selected and spiked with organophosphorus chemical warfare agents (sarin and soman) and/or their hydrolysis products (isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid) at the 10 µg/g level to assess the potential of an aqueous extraction method for soil analysis. Mass spectrometric characterization and quantitation were performed during LC-ESI-MS with a time-of-flight (TOF) instrument capable of acquiring high resolution (5000 with a 50% valley) continuum ESI-MS data on picogram quantities of analyte. Recovery of sarin and soman from the aqueous soil extracts was comparable to the existing dichloromethane extraction method used during the analysis of the Croatian soil samples, with a significant improvement in recovery being demonstrated for the chemical warfare agent hydrolysis products. The developed aqueous extraction and LC-ESI-MS analysis method appears to be an attractive alternative to the existing GC-MS based method, as soil sample extracts containing organophosphorus chemical warfare agents and/or their hydrolysis products may be analysed directly without the need for additional sample handling and derivatization steps.

Experimental

Samples

The Croatian soil samples appeared to fall into three general types and representative samples of each were selected for the development and evaluation of an aqueous extraction and analysis method. The soils were a red clay (HR005D), a tan sandy clay (HR011D) and a brown sandy clay loam (HR072D). Each of the soils (1 g) was spiked in triplicate at the 10 µg/g level using 10 µL of a 1 mg/mL chemical warfare agent and/or chemical warfare agent hydrolysis product standard mixture (in dichloromethane). The exception was the 50 µg/g spike of the soils to evaluate recovery of chemical warfare agent hydrolysis products using the existing cleanup scheme (12). Each spiked soil sample was extracted after standing one hour at 4°C using either the existing cleanup scheme (GC-MS based method) or the developed aqueous cleanup scheme (LC-ESI-MS based method).

Chemical warfare agents, their hydrolysis products and triethyl phosphate were provided by the Canadian National Single Small Scale Facility at DRES.

Existing cleanup and analysis method (GC-MS based method)

Soil samples and spiked soil samples were handled in a manner similar to a published method developed at DRES for the analysis of chemical warfare agents in soil (12). One gram of each soil sample was weighted and transferred into 16 mm × 125 mm glass culture tubes. Each soil sample was extracted with 3 mL of dichloromethane by ultrasonic vibration (10 min) and then centrifuged at 700 g for 10 min. The dichloromethane layer (1.5 mL) was removed and concentrated under a gentle stream of helium to 75 µL. One microlitre injection(s) were used for GC-MS determination of chemical warfare agents in each soil extract.

Trimethylsilylation was used to enhance the volatility of any chemical warfare agent hydrolysis products that may be associated with the soil samples. 100 µL of bis(trimethylsilyl)-trifluoroacetamide (BSTFA) and 100 µL pyridine were added to the remaining soil and dichloromethane (approximately 1.5 mL) in each culture tube. The contents were vortexed and the tube was placed in an ultrasonic bath for 10 minutes. The soil samples were then heated for 20 min at 60°C and centrifuged for 10 min at 700 g. A portion of the trimethylsilyl/ dichloromethane layer (0.5 mL) containing the derivatization reagents was removed and 1 µL aliquots were used during GC-MS analysis for the presence of chemical warfare agent hydrolysis products.

Capillary column gas chromatographic-mass spectrometric (GC-MS) analyses were performed with a Trio-1 bench-top instrument under electron impact (EI) operating conditions (emission, 0.15 mA; electron energy, 70 eV and source temperature, 200°C). Full scanning MS data were acquired with unit resolution (50% valley definition) at 1 second/scan over a 40 to 400 u mass range. GC separations were performed with a HP 5890 gas chromatograph

equipped with an on-column injector. A 15 m × 0.32 mm I.D. DB-1701 J&W capillary column (film thickness: 0.25 μm) was used for all GC-MS analyses with the following temperature program: 40°C (2 min) 10°C/min 280°C. A 1 min solvent delay was used prior to MS data acquisition for the dichloromethane extracts. A longer solvent delay, 6 min, was required for the trimethylsilyl/dichloromethane extracts to minimize MS data acquisition of the numerous solvent/derivatizing reagent components. Quantitation were performed with a HP 5890 gas chromatograph equipped with a flame ion ionization detector under similar chromatographic conditions using a 15 m × 0.53 mm I.D. DB-1701 J&W capillary column (film thickness: 1 μm).

Aqueous cleanup and analysis method (LC-ESI-MS based method)

One gram of each soil sample was weighted and transferred into 16 mm × 125 mm glass culture tubes. Each soil sample and spiked soil sample was extracted with 1 mL of water by ultrasonic vibration (10 min) and then centrifuged at 700 g for 10 min. A portion of the water layer was removed (about 200 μL) and 5 μL injection(s) were used for LC-ESI-MS determination of chemical warfare agents and/or their hydrolysis products.

ESI-MS data were acquired using a Micromass LCT time-of-flight mass spectrometer equipped with the Z-spray electrospray interface. The electrospray capillary was operated at 3.2 kV and the sampling cone voltage was either 20 or 30 volts. Nitrogen desolvation gas was introduced into the interface (80 °C) at a flow rate of 480 L/h. Nitrogen nebulizer gas was introduced at a flow rate of 66 L/h. ESI-MS data were acquired from 1000 to 70 Da (1 sec) in the continuum mode with a resolution of 5000 (50% valley definition).

LC separations were performed using an Applied Biosystems Model 140B dual syringe pump equipped with a Zorbax 150 mm × 0.32 mm I.D. C_{18} SB (5 μm) packed fused-silica capillary column and a Rheodyne 8125 injector with a 5 Paul A. D'Agostino μL sample loop. The following solvent compositions were prepared for LC separation: Solvent A (0.1% trifluoroacetic acid in water) and Solvent B (0.1% trifluoroacetic acid in acetonitrile(ACN)/water, 95:5). Chromatographic separations were performed using a 1% to 75%B gradient program over 30 minutes. In order to minimize dead volume effects and ensure reproducible mixing, the mobile phase was delivered at 200 μL/min and split prior to the injector such that the flow through the column was 16 μL/min.

Results and discussion

Croatian soil analysis

Seventy-six soil samples, collected as part of Operation Contact during the summer of 1999, were sent to DRES and analysed for the presence of chemical warfare agents and their hydrolysis products. All soil samples were handled in a manner similar to a published method developed at DRES for the analysis of chemical warfare agents in soil (12). The cleanup scheme generated two extracts for each soil sample that were each analysed by capillary column GC-MS. The dichloromethane extract was analysed for the presence of chemical warfare agents, including sarin, soman, mustrad, tabun and VX, and the trimethylsilyl/dichloromethane extract was analysed for the presence of common chemical warfare agent hydrolysis products.

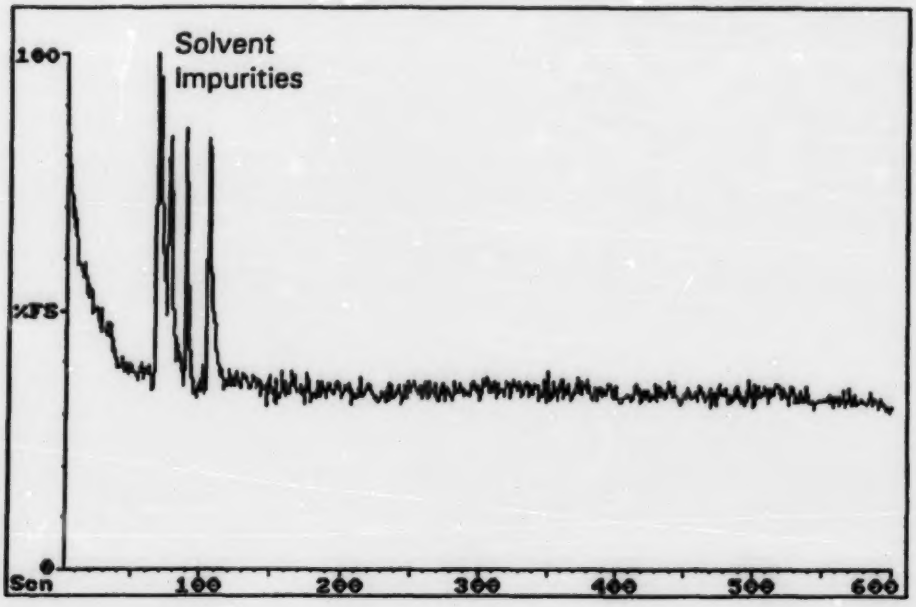

Figure 1. Capillary column GC-MS total ion current (m/z 400 to m/z 40) chromatogram obtained for a dichloromethane extract of Croatian soil sample HR011D. Four minor solvent impurities were detected following concentration of the extract. [X-axis: 1 scan number (Scn) = 1 second; Temperature program: 40°C (2 min) 10°C/min 280°C; Delay of 1 min prior to data acquisition].

Figure 1 illustrates the relevant region of a typical capillary column GC-MS total ion current chromatogram acquired for the dichloromethane extract of one of the Croatian soil samples. The sample extract was concentrated 20 fold by nitrogen blowdown to enhance the method sensitivity, resulting in a sample detection limit of 0.15 µg/g. This increased the response for several solvent impurities near the solvent front, but these components did not interfere with the chemical warfare agent analysis. Each soil sample extract total ion current chromatogram was interrogated for the presence of ions characteristic of chemical warfare agents (e.g., m/z 99 for methylphosphonofluoridates such as sarin and soman). No signal was detected for any of the diagnostic ions in the regions of the acquired GC-MS chromatograms where the chemical warfare agents would be detected in the soil sample extracts.

Figure 2 illustrates the relevant region of a typical capillary column GC-MS total ion current chromatogram obtained for the trimethylsilyl/dichloromethane extract of one of the unspiked Croatian soil samples. No signal was detected above the sample detection limit of 1.7 µg/g and no signal was detected for any of the diagnostic ions in the regions of the acquired GC-MS chromatograms where the chemical warfare agent hydrolysis products would be expected.

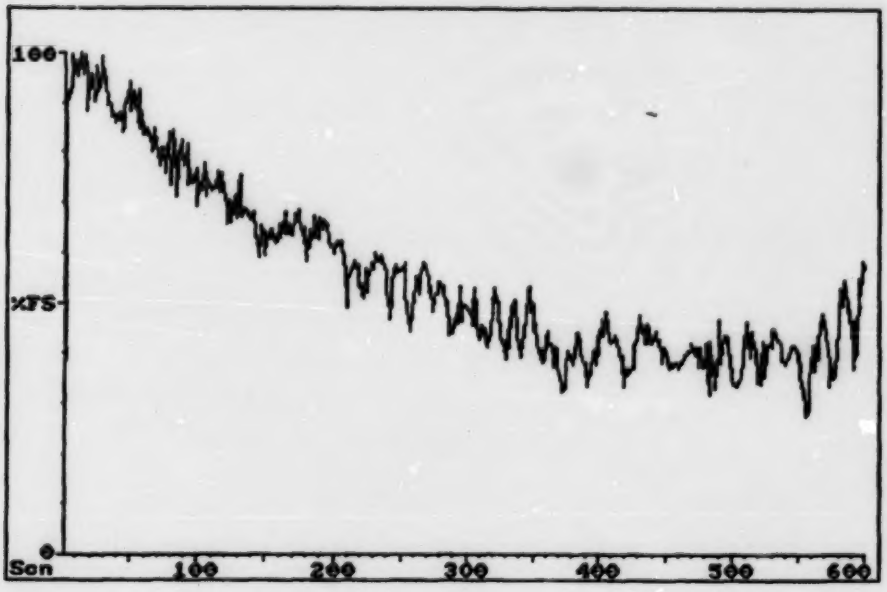

Figure 2. Capillary column GC-MS total ion current (m/z 400 to m/z 40) chromatogram obtained for Croatian soil sample HR005D following trimethylsilylation. [X-axis: 1 scan number (Scn) = 1 second; Temperature program: 40°C (2 min) 10°C/min 280°C; Delay of 6 min prior to data acquisition].

The GC-MS based method (12) used for the analysis of the Croatian soil samples utilizes dichloromethane ultrasonic extraction for the isolation of chemical warfare agents from contaminated soils. Extraction efficiency will vary with soil type, but experience has shown that most chemical warfare agents will be extracted with sufficient efficiency to enable identification. The efficiency of chemical warfare agent hydrolysis product extraction as their trimethylsilyl derivatives was not evaluated, as the focus in the early 1990's was on the qualitative observation of residual hydrolysis products resulting from hydrolysis of the spiked chemical warfare agents. With the introduction of commercial LC-ESI-MS systems, analytical methods that make use of reverse phase columns and acetonitrile or methanol/water mobile phases (isocratic or gradient programs) could be developed for the analysis of aqueous extracts or samples. Given the polarity and solubility of the chemical warfare agent hydrolysis products in water, a method utilizing aqueous ultrasonic extraction and reversed phase LC-ESI-MS analysis seemed worth investigating. If applicable, this approach would allow for direct analysis of aqueous extracts without the need for additional sample handling and derivatization. It would also eliminate the concern over the presence of moisture in soil samples, a factor that impedes the derivatization process required for GC-MS analyses.

Soil spiking experiments

The Croatian soil samples were of three general types, a red clay (e.g., HR005D), a tan sandy clay (e.g., HR011D) and a brown sandy clay loam (e.g., HR072D). A representative sample of each type was selected for the development, evaluation and comparison of an aqueous based extraction and analysis scheme with the existing cleanup scheme (12). The existing cleanup scheme was evaluated by spiking the soil samples at the 10 µg/g level with sarin, soman, mustard and triethyl phosphate or at the 50 µg/g level with isopropyl methylphosphonic acid, pinacolyl methylphosphonic acid and thiodiglycol. The extraction efficiency of each spiked compound was determined for each soil in triplicate (at a minimum) by capillary column GC-FID.

The same Croatian soil samples were also spiked with sarin, soman and their hydrolysis products, isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid, at the 10 µg/g level. Each sample was extracted with water using the developed cleanup scheme and analysed in triplicate by packed capillary LC-ESI-MS. Soil samples were also spiked with just the hydrolysis products, since hydrolysis of the spiked organophosphorus chemical warfare agents during sample extraction was anticipated. Mustard was not used during spiking experiments since, unlike organophosphorus chemical warfare agents and their hydrolysis products, it does not ionize during ESI-MS (28,29).

Table 1 summarizes the dichloromethane extraction efficiencies for the chemical warfare agents spiked at the 10 µg/g level using the existing GC-MS based method (12). All the spiked chemical warfare agents and the simulant, triethyl phosphate, were recovered from the soil samples with efficiencies that would be more than suffice for CF retrospective confirmation purposes. Recovery of soman, mustard and triethyl phosphate was determined by capillary column GC-FID (Figure 3) and exceeded 50% for all three soil types. Sarin was recovered efficiently from the tan sandy clay (approximately 60%) but was only recovered in the 20% to 30% range from the other two soil types, illustrating the importance of soil type on

recovery efficiency. These recoveries were compared to the recovery of the same compounds from Suffield range soils and were found to be somewhat higher (12).

Table 1. *Recovery of sarin, soman, triethyl phosphate and mustard from three Croatian soil samples spiked at the 10 µg/g level (dichloromethane extract). All analyses performed by capillary column GC with flame ionization detection.*

SOIL SAMPLE	PERCENT RECOVERY (MEAN ± SD)			
	Sarin	***Soman***	***Triethyl phosphate***	***Mustard***
HR005D (clay, red)	22 ± 3 (n=5)	61 ± 10 (n=5)	86 ± 8 (n =5)	81 ± 14 (n=5)
HR011D (sandy clay, tan)	63 ± 8 (n=5)	80 ± 5 (n=5)	93 ± 5 (n=5)	53 ± 5 (n=5)
HR072D (sandy clay loam, brown)	27 ± 4 (n=3)	62 ± 3 (n=3)	75 ± 3 (n=3)	80 ± 2 (n=3)

The recovery efficiency of hydrolysis products as their trimethylsilyl derivatives was not evaluated during the Suffield soil study, as the focus was strictly qualitative. Three hydrolysis products isopropyl methylphosphonic acid, pinacolyl methylphosphonic acid and thiodiglycol were spiked onto each of the Croatian soil samples at a higher level than the chemical warfare agents, 50 µg/g, since these were significant chemical interferences associated with derivatization procedure (numerous chromatographic peaks without numbers in Figure 3). Table 2 summarizes the recovery efficiencies for each hydrolysis product and Figure 4 illustrates typical capillary column GC-FID chromatograms used for quantitative purposes. All three hydrolysis products were only recovered from the tan sandy clay sample (recovery efficiency in the 30% to 60% range). Only thiodiglycol was recovered from the remaining two soil types. Method improvement or development of a new method would be required to reliably detect and confirm the chemical warfare agent hydrolysis products in these soil types.

Table 2. *Recovery of isopropyl methylphosphonic acid (iPrMPA) pinacolyl methylphosphonic acid (PinMPA) and thiodiglycol from three Croatian soil samples spiked at the 50 µg/g level (trimethylsilyl/dichloromethane extract) All analyses performed by capillary column GC with flame ionization detection.*

SOIL SAMPLE	PERCENT RECOVERY (MEAN ± SD)		
	iPrMPA	***PinMPA***	***Thidiglycol***
HR005D (clay, red)	Not detected	Not detected	10 ± 1 (n=3)
HR011D (sandy clay, tan)	36 ± 9 (n=3)	34 ± 2 (n=3)	53 ± 5 (n=3)
HR072D (sandy clay loam, brown)	Not detected	Not detected	11 ± 2 (n=3)

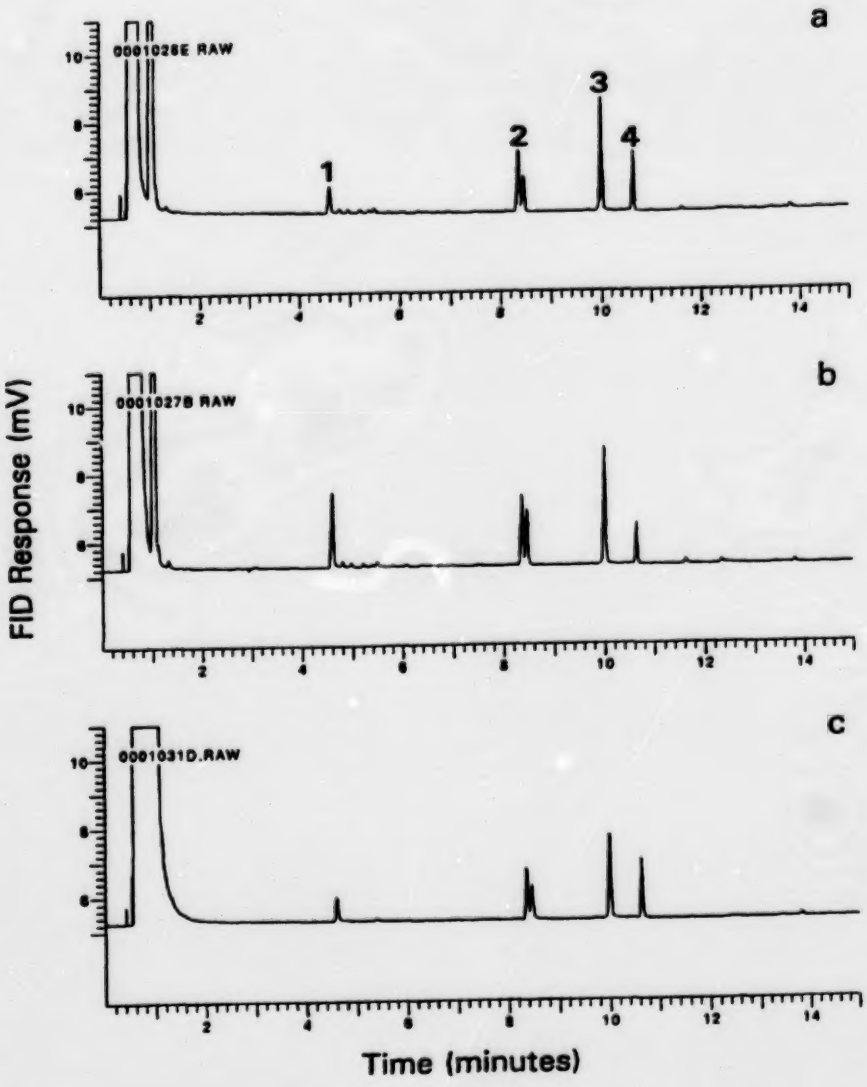

Figure 3. *Capillary column GC-FID chromatograms obtained for dichloromethane extract of a) a red clay (HR005D), b) a tan sandy clay (HR011D) and c) a brown sandy clay loam (HR072D) soil sample spiked at the 10 µg/g level with sarin (1), soman (2), triethyl phosphate (3) and mustard (4).*

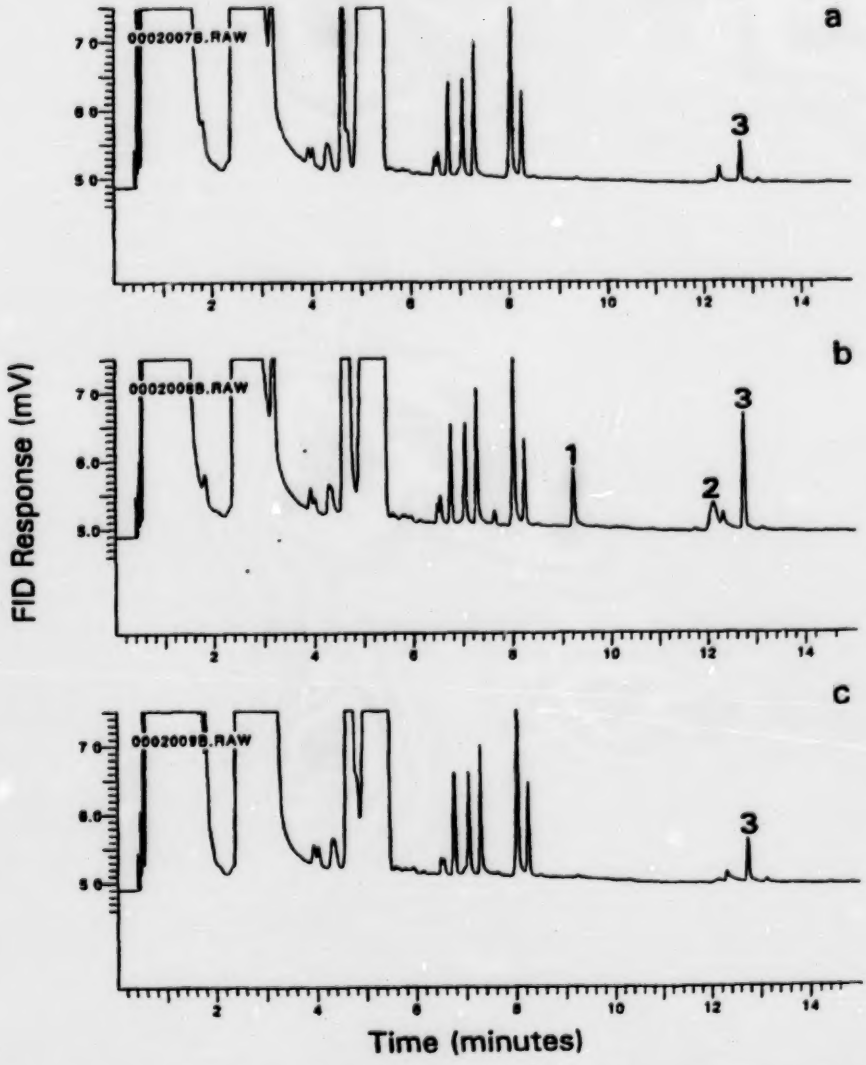

Figure 4. Capillary column GC-FID chromatograms obtained for trimethylsilyl dichloromethane extract of a) a red clay (HR005D), b) a tan sandy clay (HR011D) and c) a brown sandy clay loam (HR072D) soil sample spiked at the 50 µg/g level with isopropyl methylphosphonic acid (1), pinacolyl methylphosphonic acid (2) and thiodiglycol (3)

Several previous DRES studies indicated the utility of packed capillary LC-ESI-MS for the detection and identification of organophosphorus chemical warfare agent, their hydrolysis products and related compounds in aqueous samples (28,29). Extraction of both the organophosphorus chemical warfare agents and their hydrolysis products with water from soil would be an attractive alternative as the aqueous extracts could be analysed directly by packed capillary LC-ESI-MS. This approach was initially investigated by extracting each of the soil samples with water, to provide an indication as to what other chemical(s) would be co-extracted. Figure 5 illustrates the packed capillary LC-ESI-MS total ion current chromatogram of the brown sandy clay loam aqueous extract obtained under gradient programming conditions. The chromatograms for all three soils were similar in that they contained a major component(s) eluting in the first few minutes. The mass spectrum obtained for the broad chromatographic peak (inset in Figure 5) was similar in ion content for all three soil sample extracts, although the relative intensities of the ions varied somewhat. No attempt was made to identify the component(s) in the acquired mass spectrum.

All three soil types were then spiked at the 10 µg/g level with sarin, soman and their hydrolysis products, isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid. Recovery data for sarin and soman were remarkably similar to the data obtained for their extraction with dichloromethane (Table 3), with the poorest extraction efficiency being for sarin from the red clay and brown sandy clay loam soil types. Figure 6 illustrates typical packed capillary LC-ESI-MS total ion current chromatograms obtained for aqueous extracts of each of the spiked soil samples. This new cleanup and analysis approach could be used for chemical warfare agent analysis provided only organophosphorus chemical warfare agent contamination was suspected. Mustard cannot be detected by ESI-MS, although the many hydrolysis products of munitions grade mustard may be identified using this approach (27).

Table 3. *Recovery of sarin, soman, isopropyl methylphosphonic acid (iPrMPA) and pinacolyl methylphosphonic acid (PinMPA) from three Croatian soil samples spiked at the 10 µg/g level (aqueous extract). All analyses performed by packed capillary LC with electrospray mass spectrometric detection.*

SOIL SAMPLE	PERCENT RECOVERY (MEAN ± SD)			
	Sarin	***Soman***	***IPrMPA***	***PinMPA***
HR005D (clay, red)	19 ± 9 (n=3)	57 ± 12 (n=3)	160 ± 17 (n=3)[1]	136 ± 12 (n=3)[1]
HR011D (sandy clay, tan)	77 ± 11 (n=3)	86 ± 10 (n=3)	124 ± 7 (n=3)[1]	116 ± 17 (n=3)[1]
HR072D (sandy clay loam, brown)	27 ± 4 (n=3)	52 ± 6 (n=3)	171 ± 11 (n=3)[1]	145 ± 12 (n=3)[1]

[1] Note Recoveries of isopropyl methylphosphonic acid (iPrMPA) and pinacolyl methylphosphonic acid (PinMPA) greater than 100% due to hydrolysis of sarin and soman, respectively

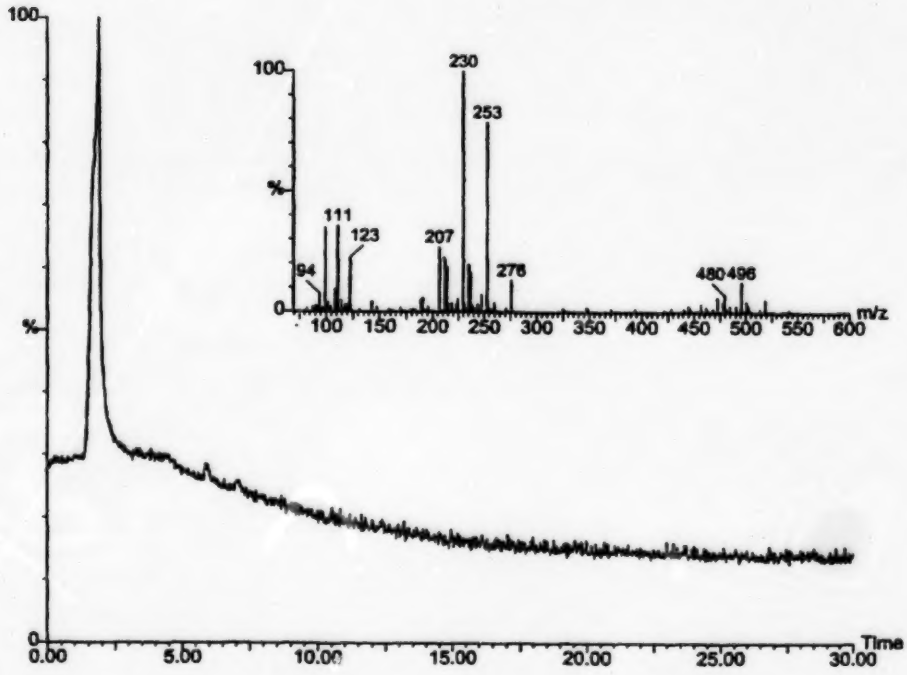

Figure 5. *Packed capillary LC-ESI-MS total ion current (m/z 400 to m/z 85) chromatogram obtained for an aqueous extract of a brown sandy clay loam (HR072D) soil sample. Inset: ESI-MS data for components in the major chromatographic peak.*

A large chromatographic peak was observed in the first few minutes of each chromatogram, consistent with the initial aqueous extract of the each soil sample (refer to Figure 5). All four spiked compounds were readily detected and identified based on their acquired ESI-MS data (Figure 7). The spiked compounds exhibited $(M+H)^+$, $(M+H+ACN)^+$ ions and/or protonated dimers that could be used to confirm molecular mass and product ions resulting from alkene loss from the alkoxy substituents (and their acetonitrile adducts). The only anomaly noted during the analysis was the detection of two chromatographic peaks with identical mass spectra for isopropyl methylphosphonic acid. Peak splitting caused by the co-extracted soil sample components or the formation/presence of another isomer (e.g., n-propyl) was suspected.

The recovery of hydrolysis products was almost quantitative with recoveries in excess of 80% for all three soil sample types (Table 3). In all cases the sum of the chemical warfare agent and hydrolysis product percentages accounted for nearly all the compound(s) used. Recovery percentages for the both hydrolysis products exceeded 100% in Table III due to hydrolysis of

a portion of the sarin and soman during sample standing and/or cleanup. This was verified during a single spiking experiment using only the two hydrolysis products (Table 4). Isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid were recovered form the soils with efficiencies ranging from 80% to 101%, and 87% to 110%, respectively. These recoveries were much better than those found using the existing derivatization procedure and use of this new cleanup scheme would be recommended for the verification of the chemical warfare agent hydrolysis products in contaminated soil samples.

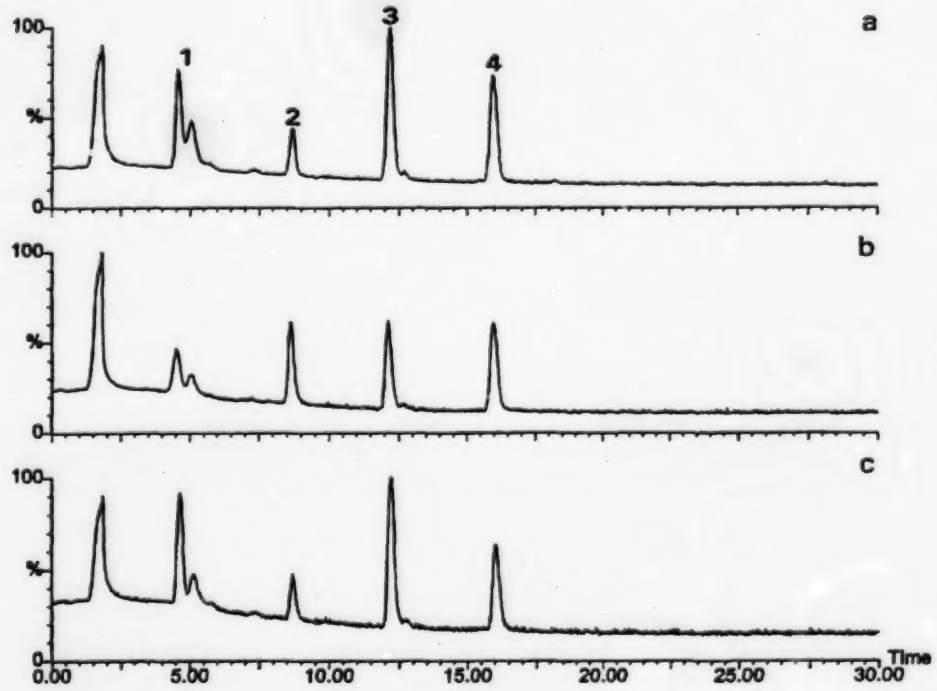

Figure 6. Packed capillary LC-ESI-MS total ion current (m/z 400 to m/z 85) chromatograms obtained for an aqueous extract of a) a red clay (HR005D), b) a tan sandy clay (HR011D) and c) a brown sandy clay loam (HR072D) soil sample spiked at the 10 µg/g level with isopropyl methylphosphonic acid (1), sarin (2), pinacolyl methylphosphonic acid (3) and soman (4).

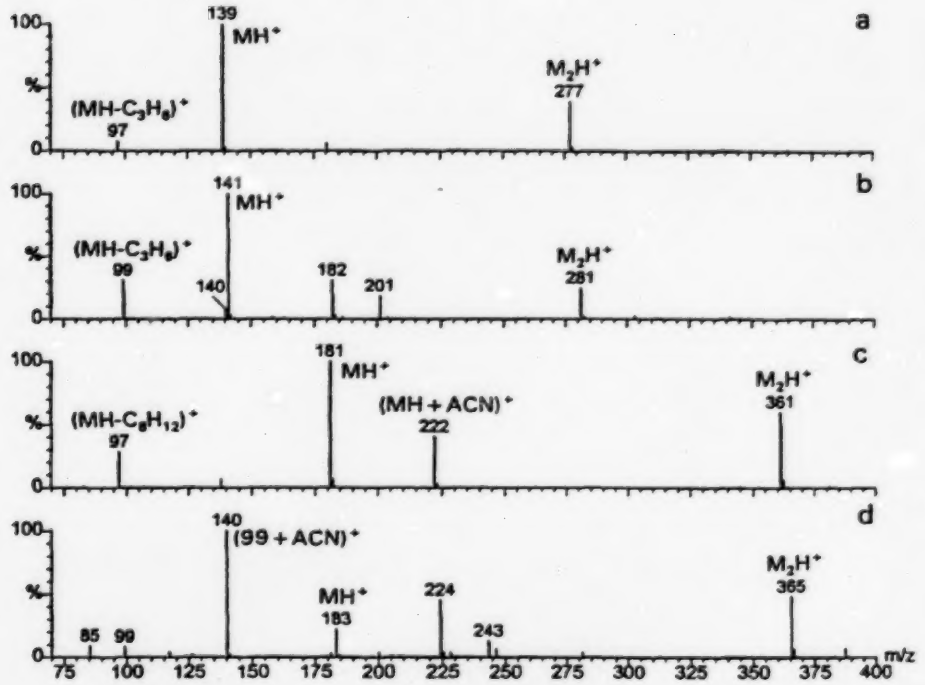

Figure 7. *Typical ESI-MS data (sampling cone voltage: 20 V) obtained for a) isopropyl methylphosphonic acid, b) sarin, c) pinacolyl methylphosphonic acid and d) soman during analysis of aqueous soil extracts.*

Table 4. *Recovery of isopropyl methylphosphonic acid (iPrMPA) and pinacolyl methylphosphonic acid (PinMPA) from three Croatian soil samples spiked at the 10 µg/g level (aqueous extract). All analyses performed by packed capillary LC with electrospray mass spectrometric detection.*

SOIL SAMPLE	PERCENT RECOVERY (MEAN ± SD)	
	iPrMPA	*PinMPA*
HR005D (clay, red)	80	87
HR011D (sandy clay, tan)	98	104
HR072D (sandy clay loam, brown)	101	110

Conclusions

An analytical method based on aqueous extraction and gradient-programming packed capillary LC-ESI-MS analysis was developed for the determination of trace levels of organophosphorus chemical warfare agents and their hydrolysis products in contaminated soil samples. Three different Croatian soils, a red clay, a tan sandy loam and a brown sandy clay loam, were selected and spiked with sarin and soman and their hydrolysis products, isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid, at the 10 µg/g level to assess the efficiency of the aqueous extraction method for contaminated soil analysis. LC-ESI-MS characterization and quantitation was performed with a time-of-flight (TOF) instrument capable of acquiring high resolution continuum data on picogram quantities of analyte. Full mass spectra were acquired for each compound, with all spiked compounds exhibiting $(M+H)^+$, $(M+H+ACN)^+$ ions and/or protonated dimers that could be used to confirm molecular mass and product ions resulting from alkene loss from the alkoxy substituents (and their acetonitrile adducts).

Recovery of sarin and soman from the aqueous soil extracts was comparable to the existing dichloromethane extraction method used during the analysis of the Croatian soil samples. However a significant improvement in recovery was demonstrated for the recovery of chemical warfare agent hydrolysis products from the same soil samples. Sarin and soman were recovered in the 20% to 90% range from the three soil types with the aqueous extraction cleanup scheme, while their hydrolysis products were extracted almost quantitatively, with recoveries in excess of 80% for all three soil types. The developed aqueous extraction and LC-ESI-MS analysis method appears to be an attractive alternative to the existing GC-MS based method, particularly when organophosphorus chemical warfare agent hydrolysis products require determination. Aqueous extracts of soil samples contaminated with organophosphorus chemical warfare agents and/or their hydrolysis products may be analysed directly during a single analysis, without the additional sample handling and derivatization required by the GC-MS based method for hydrolysis product determination.

The reported analytical method represents a significant improvement over the existing GC-MS based method for the determination of organophosphorus chemical warfare agent hydrolysis products in contaminated soils. It complements the existing GC-MS based method for organophosphoprus chemical warfare agent determination, providing the analyst with similar recovery efficiencies and molecular mass data. The analytical method would be valuable for the identification of these compounds in contaminated soil samples and will be employed in the future during the analysis of suspect soil samples collected by the Canadian Forces.

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Determination of Organophosphorus Chemical Warfare Agents and their Hydrolysis Products in Soil by Packed Capillary Liquid Chromatography-Electrospray Mass Spectrometry (PC-ESI-MS)

4 AUTHORS (Last name, first name, middle initial. If military, show rank, e.g. Doe, Maj. John E)

D'Agostino, Paul A., Hancock, James R. and Provost, Lionel R.

5 DATE OF PUBLICATION (month and year of publication of document)

June 2000

6a. NO. OF PAGES (total containing information, include Annexes, Appendices, etc) 19

6b. NO OF REFS (total cited in document) 29

7 DESCRIPTIVE NOTES (the category of the document, e g. technical report, technical note or memorandum. If appropriate, enter the type of report, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.)

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8 SPONSORING ACTIVITY (the name of the department project office or laboratory sponsoring the research and development Include the address)

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9a. PROJECT OR GRANT NO. (If appropriate, the applicable research and development project or grant number under which the document was written Please specify whether project or grant.)

9b CONTRACT NO (If appropriate, the applicable number under which the document was written.)

10a. ORIGINATOR'S DOCUMENT NUMBER (the official document number by which the document is identified by the originating activity This number must be unique to this document.)

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An analytical method based on aqueous ultrasonic extraction and packed capillary LC-ESI-MS analysis was developed and compared to the existing GC-MS based method for the trace determination of organophosphorus chemical warfare agents and their hydrolysis products in contaminated soil. Three soils, a red clay, a tan sandy loam and a brown sandy clay loam, were selected and spiked with sarin and soman and their hydrolysis products, isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid, at the 10 μg/g level to assess recovery efficiency. Recovery of sarin and soman from the aqueous soil extracts was comparable to the existing analytical method, with a significant improvement in recovery being demonstrated for the chemical warfare agent hydrolysis products. Sarin and soman were recovered in the 20% to 90% range from the three soil types with aqueous extraction, while the hydrolysis products of these chemical warfare agents were extracted almost quantitatively, with recoveries in excess of 80% for all three soil types. The developed soil extraction and analysis method appears to be an attractive alternative to the GC-MS based method, since aqueous extracts containing chemical warfare agent hydrolysis products may be analysed directly, eliminating the need for additional sample handling and derivatization steps.

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